THE THERMAL REACTIONS OF SOME ADVANCED SOLID OXIDIZERS

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INTRODUCTION

The perchlorates of hydrazine, namely, hydrazinium monoperchlorate ($N_2H_5ClO_4$) and hydrazinium diperchlorate ($N_2H_5(ClO_4)_2$) are receiving increasing attention as high energy solid propellant ingredients. While both of these compounds have been known for some time, very little has appeared concerning their thermal reactions.

The monoperchlorate was first reported by Salvadori in 1907 (Ref 1). He reported decomposition after prolonged heating at 131-132°, a rapid increase in rate with increased temperature, and explosion at 240°. Barlot and Marsule (Ref 2) reported decomposition beginning at 145°. The most recent information was reported by Shidlovskii, Semishin and Shmagin (Ref 3) who studied weight loss at temperatures from 160° to 250°. The dihydrate of hydrazinium diperchlorate was reported by Turrentine in 1915 (Ref 4), however, there is no information reported on the properties of the anhydrous material.

In our program to elucidate the chemistry of these important compounds, we have examined their thermal reactions as a first step.

EXPERIMENTAL

A. Materials

Hydrazinium Diperchlorate (HP-2)

The HP-2 used in this study consisted of uniform small crystals (0.3 to 0.8 mm). Its purity was determined by a potentiometric titration with a standard base. The major impurities were hydrazine (mono-) perchlorate or free perchloric acid. Their presence depended on the extent of drying and the precise balance was difficult to maintain. Examples of the purity of various batches used are shown in Table I.

TABLE I

ANALYSIS OF VARIOUS HP-2 SAMPLES

Batch No.	% HP-2	% Impurity
1	99.86	0.42 - HP
2	99.89	0.26 - HP
3	99.79	0.15 - $HClO_4$
4	99.37	0.15 - HP
5	99.58	0.04 - $HClO_4$

Hydrazinium Monoperchlorate (HP)

High purity HP was prepared by neutralizing 60% $HClO_4$ with 75% N_2H_4 at temperatures from 0°-25°. The salt precipitated from water at 0° and was filtered cold in scintered glass funnels. The fine white crystals were gently removed from the filter with a Teflon spatula and placed in a drying tube at 70° for two hours at a constant vacuum of 0.05 mm Hg to break down the hemihydrate. Samples were titrated either potentiometrically or with phenolphthalien indicator by 0.1000 N. NaOH. Characteristic purity factors range from 99.83% to 99.94%.

B. Apparatus and Procedure

The decompositions were followed manometrically by monitoring pressure rise at constant temperature in a constant volume reactor. The apparatus was fabricated completely of glass and contained a thin glass membrane which was used for sensing pressure. A diagram of the apparatus is shown in Figure 1. A glass pointer was fused to the diaphragm and the apparatus was used as a null device by adjusting the pressure in the external volume until the pointer came to rest at the reference mark. The sensitivity of the gauge varied from one diaphragm to another, however, all gave perceptible deflections of the pointer for pressure differentials of 1 mm.

At the completion of the reaction, gas samples were collected through the break-off seal and analyzed on the mass spectrometer. Condensed phase residues were analyzed by conventional wet analytical techniques.

RESULTS AND DISCUSSION
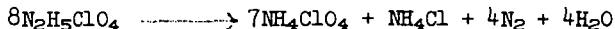
A. General Nature of the Reaction

In a sealed system the reaction of HP-2 is characterized by an induction period, during which time a gradual pressure rise is observed. At the end of the induction period the reaction accelerates very sharply and complete decomposition results. A typical pressure vs time curve is shown in Figure 2. The initial phase of the HP reaction is also acceleratory, however, there is no sign of the acceleration of the type characteristic of HP-2. A typical pressure vs time curve for HP is shown in Figure 3.

B. Stoichiometry

Analysis of the vapor and condensed products of the overall HP-2 reaction indicate the following stoichiometry.

$$12N_2H_6(ClO_4)_2 \longrightarrow 4NH_4ClO_4 + 12HClO_4 + 22H_2O + 10N_2 + 5O_2 + 4Cl_2$$
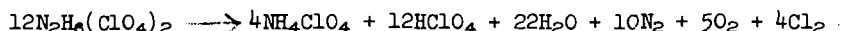
The overall stoichiometry of the HP reaction is:

$$8N_2H_5ClO_4 \longrightarrow 7NH_4ClO_4 + NH_4Cl + 4N_2 + 4H_2O$$

C. Rate Measurements

Hydrazinium Diperchlorate

For the case of HP_2 there is a very sharp transition at the initiation of the accelerated phase. The assumption was made that when the reaction goes into the accelerated phase the concentrations of all reacting species are equal.

Thus the expression for the rate of disappearance of HP-2 may be written as follows:

$$\frac{-d\,[HP\text{-}2]}{dt} = kf(C) \tag{1}$$

where k is the specific rate constant and f(C) is some function of the concentration of reactants.

Integration of (1) gives

$$kt_i = f'(C_i) \tag{2}$$

the subscript $_i$ represents the initiation of the accelerated phase of decomposition.

The assumption is made that at t_i, the concentrations of all reactants are equal and $f'(C_i)$ is constant. Thus the time to acceleration is inversely proportional to the specific rate constant.

$$1/t_i = k_0k \tag{3}$$

where $1/k_0$ is $f'(C_i)$.

In any series of experiments the rates of reaction were compared on the basis of k_0k or $1/t_i$.

Hydrazinium Monoperchlorate

The reaction of HP is not characterized by the same type of rapid acceleration as is found for HP-2. Rather the first 10% of reaction is acceleratory following the expression

$$N/No = At^2$$

where η = number of moles of gaseous products
No = number of moles of HP originally present
t = time in minutes

The rate of reaction remains constant from approximately 10% to 70% decomposition and is given by the following expression:

$$\eta/No = C(t-D)$$

For comparison of rates at various temperatures the linear portion of the curve was used.

D. Effect of Temperature

The time to acceleration (t_i) for HP-2 is shown as a function of temperature in Table II.

TABLE II

TIME TO ACCELERATION AS A FUNCTION OF TEMPERATURE

Temperature ($^{\circ}$C)	Induction Period (hrs)
120	77
130	32
140	22
150	9

The dependence of reaction rate on temperature is given by the Arrhenius relationship

$$k = Ae^{-E/RT} \qquad (4)$$

Substituting for the specific rate constant from (3) gives:

$$1/t_i = k_oAe^{-E/RT} \qquad (5)$$

or $$\ln(1/t_i) = \ln(k_oA) - E/RT \qquad (6)$$

For HP-2 between 100 and 150°C the relationship between $1/t_i$ and temperature is:

$$\log 1/t_i = 11.203 - \frac{5,143}{T(^{\circ}K)}$$

and the activation energy, E, is 23.5 kcal/mole.

The effect of temperature on the decomposition rate of HP is shown in Table III. The table gives the values of A, C and D which are the parameters of the power expression:

$$\eta/N_0 = At^2 \qquad\qquad 0 > \eta/N_0 > 0.1$$

and the linear expression:

$$\eta/N_0 = C(t-D) \qquad\qquad 0.1 > \eta/N_0 > 0.7$$

Values of t_i (time of transition from the power law to the linear law) and values of η/N_0 at t_i are also given.

TABLE III

TEMPERATURE EFFECT OF HP DECOMPOSITION

T °C	A X 10^8	C X 10^4	D	t_i*	η/N_0 at t_i*
140	6.25	1.31	552	1200	0.090
150	22.9	3.25	320	480	0.080
158	107	6.9	166	300	0.090
170	260	10.9	104	170	0.070
181	1070	21.0	53	95	0.090
200	18,000	86.0	10	27	0.140

*Approximate values–time in minutes.

A plot of values of log C versus $1/T^{\circ}K$ gives an activation energy for the linear portion of the curve of 23.8 kcal/mole from 140°C to 200°C.

E. Effect of Reaction Products

The reaction of HP-2 is self accelerating and suggests autocatalysis by reaction products. The effect of two of the reaction products are given below.

1. Perchloric Acid Dihydrate

The addition of perchloric acid dihydrate has the effect of accelerating the decomposition of HP-2. The exact effect in terms of the time to acceleration ($1/t_i$) is given by the following expression.

$$1/t_i = k_0k_1 + k_0k_2 \left[HClO_4 \cdot 2H_2O\right]$$

at 140°, $k_0k_1 = 0.04$ hr^{-1} which is the rate of the reaction in the absence of additive and $k_0k_2 = 0.04$ hr^{-1} (wt %)$^{-1}$.

Thus the rate of the reaction is doubled when one percent of the acid dihydrate is added.

2. Anhydrous Perchloric Acid

The addition of anhydrous perchloric acid accelerates the reaction of HP-2 to such an extent that it exceeds the capacity of the experimental technique at 140°. Using the above convention, however, it was possible to determine a lower limit on the value of the rate constant k_0k_2. At 140° the value of k_0k_2 is greater than 2.5 hr^{-1} (wt %)$^{-1}$. Thus the rate of HP-2 decomposition is increased by a factor of at least 60 when one percent of anhydrous $HClO_4$ is present.

F. Reaction Mechanism

The initial step in the decomposition of HP-2 is the dissociation to HP and perchloric acid:

$$N_2H_5ClO_4 \cdot HClO_4 \rightleftarrows N_2H_5ClO_4 + HClO_4$$
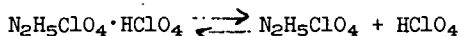
This step was verified by isolation of anhydrous $HClO_4$ as the only vapor phase specie during the early phases of the reaction. The equilibrium constants in terms of the pressure of $HClO_4$ were determined as a function of temperature and are given by the following expression.

$$\log P_{(mm)} = 22.86 - \frac{8,650}{T\ (^\circ K)} \qquad 100^\circ \text{ to } 140^\circ C$$

and the heat of dissociation is 37 kcal/mole.

The initial step of the HP decomposition is a proton transfer to produce free hydrazine and anhydrous perchloric acid:

$$N_2H_5ClO_4 \rightleftarrows N_2H_4 + HClO_4$$
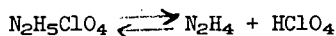
The dissociation pressures for this reaction could not be measured directly in the Sickle gauge apparatus. No dissociation pressure could be detected to 150°. At higher temperatures the decomposition was too rapid to attain equilibrium.

The initial dissociation in both cases is followed by decomposition of $HClO_4$ since it is considerably less stable than HP-2 or HP.

The reaction of anhydrous $HClO_4$ has been studied by Levy (Ref 5). At high temperatures (above 300°) the vapor phase reaction is a homogeneous one. Below approximately $300^\circ C$ the reaction is a heterogeneous one, the rate of which depends on the nature of the surface with which it is in contact. Zinov'ev and Tsentsiper (Ref 6) report an activation energy of 22.2 kcal/mole for the low temperature reaction. The similarity of the temperature coefficient of the HP, HP-2 and $HClO_4$ reactions suggest that the decomposition of $HClO_4$ may be the controlling step in each case.

Since the decomposition of $HClO_4$ is mainly a heterogeneous one in the temperature range of interest, tests were performed to determine the effect of

surface on the HP-2 reaction. The Pyrex surface was increased by the addition of known quantities of Pyrex micro spheres. These were intimately mixed with the reactant. The presence of the glass surface increased the rate. The overall rate of the heterogeneous reaction is given by the following expression:
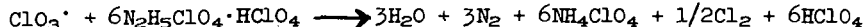
$$1/t_i = k_o k_1 + \sum k_o k_j [S_j]$$

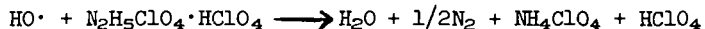where $k_o k_1$ is the rate in the absence of added surface; k_j is the specific rate constant on surface j and S_j is the surface area of the jth surface.

At 140° on Pyrex glass the value of $k_o k_{Pyrex}$ is 0.005 hr^{-1} $(cm^2)^{-1}$. Thus the heterogeneous nature of the reaction is important and this further suggests that the decomposition of $HClO_4$ is a controlling step in the reaction.

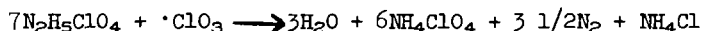At 140° the perchloric acid decomposes on a surface as follows:

$$HClO_4 \longrightarrow HO^\cdot + {}^\cdot ClO_3$$

Only the two products formed by the initial dissociation of $HClO_4$ are shown. Many other active oxidizing species such as ClO_2, ClO_4, Cl_2O_3, are undoubtedly also formed. The oxidizing species formed can oxidize the hydrazine moiety of HP-2 to ammonia thereby releasing a mole of perchloric acid. The reaction is illustrated below for the $HO^\cdot$ and $ClO_3^\cdot$ radicals. The same overall results are obtained with other oxidizing intermediates.

$$HO^\cdot + N_2H_5ClO_4 \cdot HClO_4 \longrightarrow H_2O + 1/2N_2 + NH_4ClO_4 + HClO_4$$

$$ClO_3^\cdot + 6N_2H_5ClO_4 \cdot HClO_4 \longrightarrow 3H_2O + 3N_2 + 6NH_4ClO_4 + 1/2Cl_2 + 6HClO_4$$

Each mole of perchloric acid has the capacity to oxidize seven moles of hydrazine which in turn releases seven additional moles of perchloric acid. Such a rapid chain-branching step can account for the rapid transition from the slow preacceleration phase of the reaction to the rapid acceleration.

The suggested reactions are also consistent with the fact that HP does not accelerate rapidly. Oxidizing intermediates formed by the decomposition of $HClO_4$ react with HP as follows.

$$N_2H_5ClO_4 + {}^\cdot OH \longrightarrow H_2O + NH_4ClO_4 + 1/2N_2$$

$$7N_2H_5ClO_4 + {}^\cdot ClO_3 \longrightarrow 3H_2O + 6NH_4ClO_4 + 3\ 1/2N_2 + NH_4Cl$$

An approximate kinetic expression based on the above consideration in which all oxidizing species are included, reduces to:

$$\frac{dn}{dt} = [HP] (k_1 [OH] + k_2 [ClO_3] + \ldots k_i [O_i])$$

This expression shows that the rate of gas evolution should increase until steady state concentrations of all oxidizing species are reached. After this time (t_i) the concentrations of oxidizing intermediates remain constant and are dependent on the equilibrium dissociation pressure of HP at the experimental temperature. The rate then remains constant until the HP becomes depleted.

SUMMARY AND CONCLUSIONS

The initial step in the thermal decomposition of HP-2 and HP is the dissociation of the acid-base complex to give free perchloric acid. The subsequent decomposition of perchloric acid controls the rate of the overall reaction.

In the case of HP-2 the reaction is self-accelerating due to autocatalysis by reaction products. The general form of the reaction sequence is as follows:

$$A \xrightarrow{k_1} B + \text{Products}$$

$$7A + B \xrightarrow{k_2} 7B + \text{Products}$$
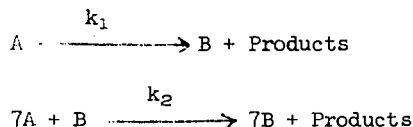
The large branching coefficient (7) and the fact that $k_2 > k_1$ leads to a very sharp transition from a slow preacceleration reaction to a rapid accelerated phase.

The HP reaction differs from that of HP-2 in that no autocatalysis is involved. The initial rate of the HP reaction does increase as active oxidizing intermediates are built up, but after a steady state concentration is reached the rate remains constant until the concentration of HP becomes depleted.

ACKNOWLEDGEMENT

REFERENCES

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3. Shidlovskii, A. A., Semishin, V. I., and Shmagin, L. F. Zhur. Priklad. Khim. 35, No. 4, 756 (1962).

4. Turrentine, J. W. and Gill, A. C. JACS, 37, 1122 (1915).

5. Levy, J. B. J. Phys. Chem., 66, 1092 (June 1962).

6. Zinov'ev, A. A., and Tsentsiper, A. B. Zhur. Neorg. Khim., 4, 724 (1959).

Atmosphere

Vacuum and
Manometer

Needle Valves
Fisher-Porter
Cat. No. 795-500

Reference wire
(anchored in epoxy)

40/50 ST Joint

Needle mounted on
pressure sensitive
diaphragm

Gas Sampling
Arm

Loading Arm

Vacuum

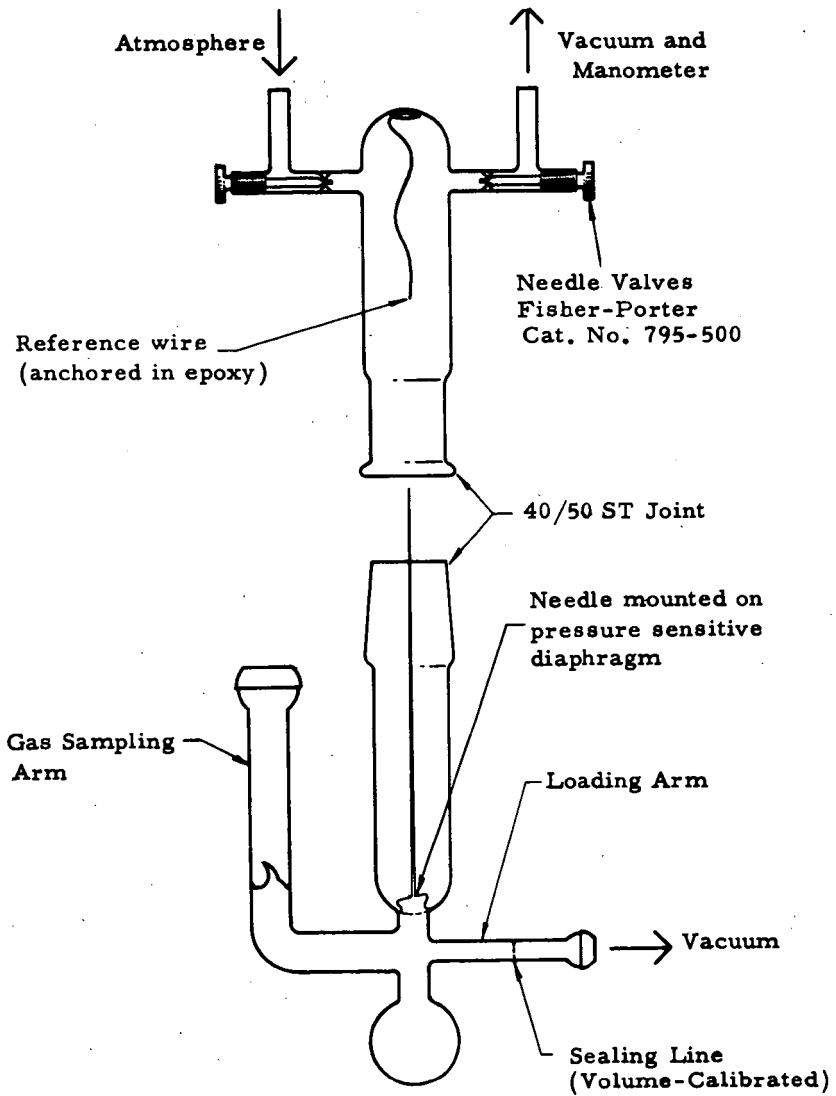Sealing Line
(Volume-Calibrated)

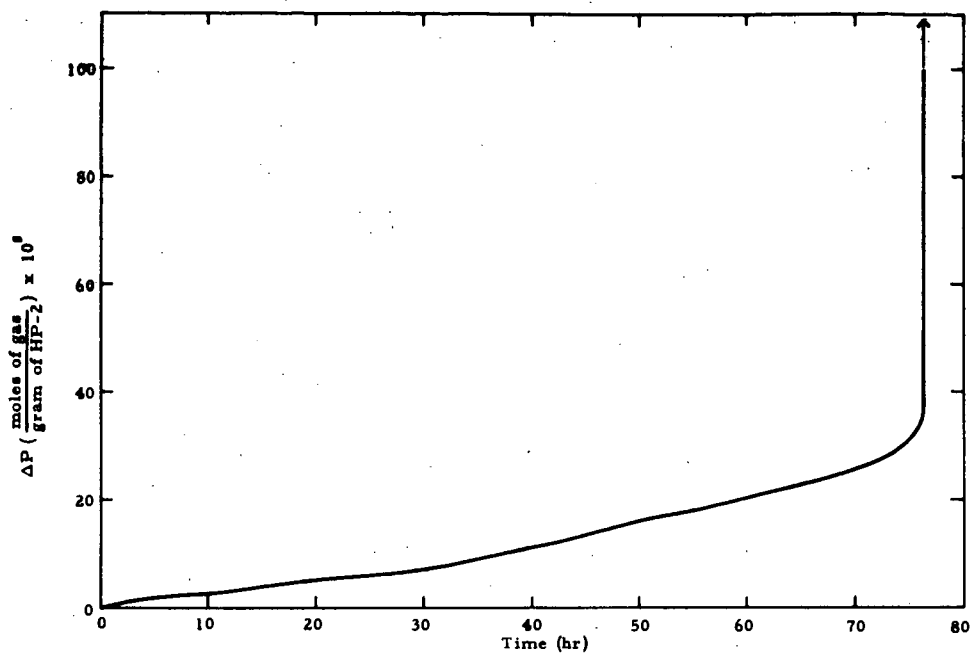Figure 1. Sickle Gauge Apparatus

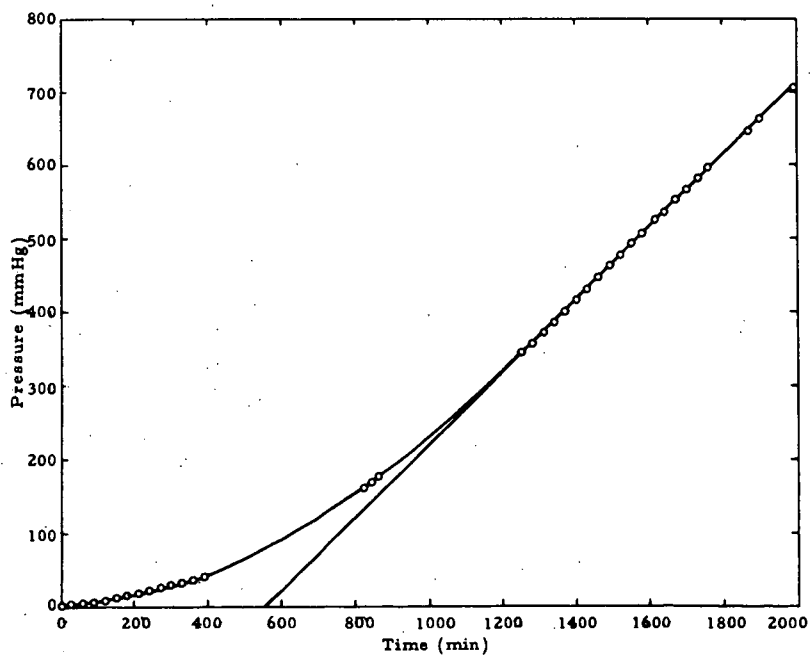Figure 2. Pressure vs Time Curve for Hydrazinium Diperchlorate at 140°C

Figure 3. Pressure vs Time Curve for Hydrazinium Perchlorate at 140°C